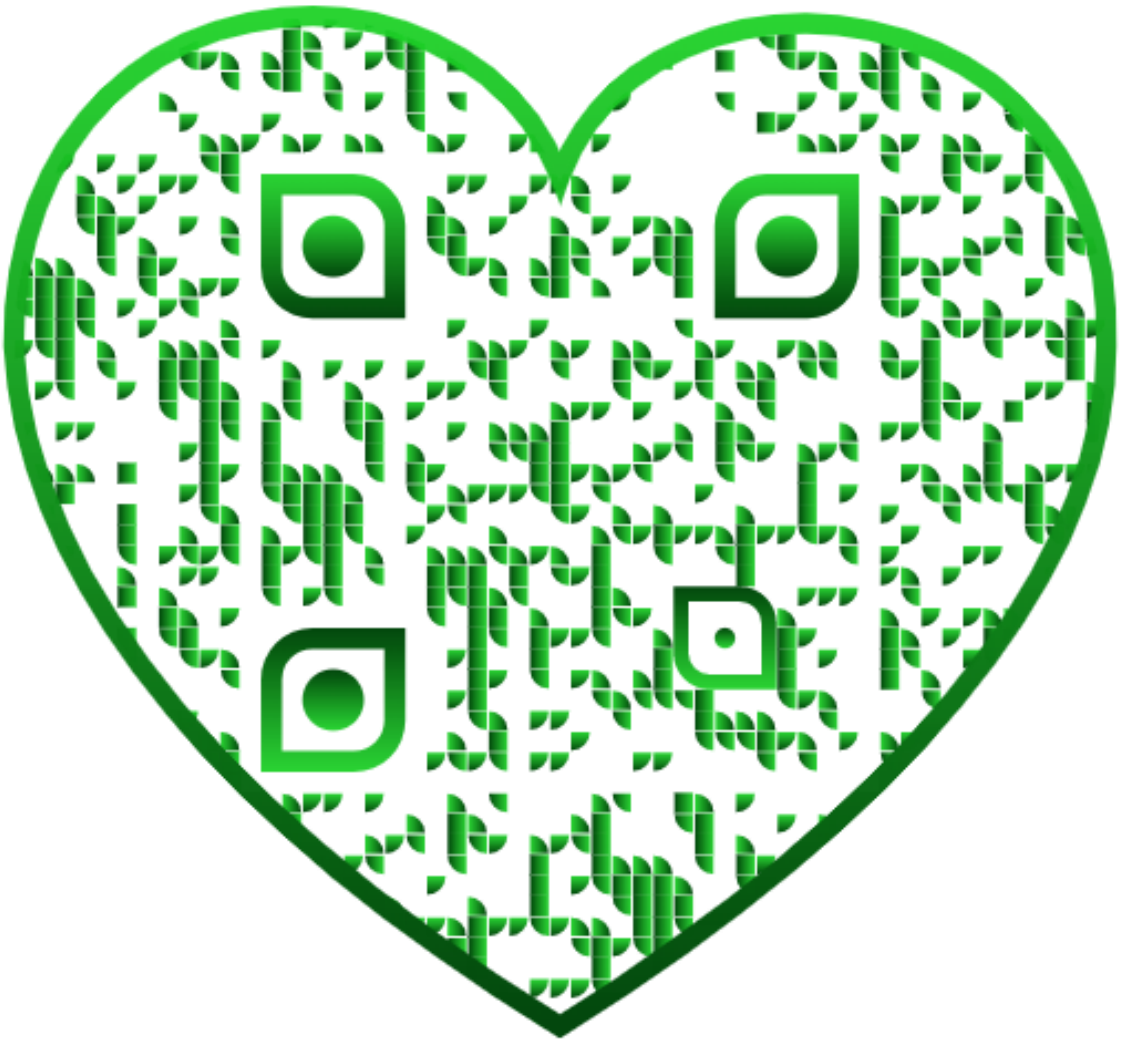
REDOX TITRATIONS



Objectives:

- At the end of this lesson the students are able to
  - describe the **principle** of redox titration
  - identify **indicators** used in redox titration
  - explain d/f **methods** of redox titration
  - describe the **quantitative** pharmaceutical **application** of redox titration

Introduction

- The volumetric analysis which are based on neutralization, precipitation and complexometric titrations involve ion combination reactions.
- On the other hand, **oxidation- reduction** method of analysis involve a change in valence by **transferring electrons** from one substance to other, termed electron transfer rxn.

- **Oxidation:** - loss of electron (↑ in oxidation number)
  - Addition of oxygen, such as $SO_2 + O \rightarrow SO_3$
  - Removal of hydrogen, e.g. $H_2S + O \rightarrow H_2O + S$
- **Reduction:** - gain of electron (↓ in oxidation number)
  - Addition of hydrogen e.g. $CH{\equiv}CH + 2H \rightarrow CH_2 = CH_2$
  - Removal of oxygen, e.g. . $CuO + 2H \rightarrow Cu + H_2O$

- A reducing agent
  - is one which loses the electrons, i.e reduces the other substance by donating electrons to it.

$$Fe^{2+} \longrightarrow Fe^{3+} + e$$
$$Ce^{3+} \longrightarrow Ce^{4+} + e$$

- An oxidaizing agent;
  - is is one which accepts electrons, i.e oxidizes the other substance by stripping off electrons from it.

$$Ce^{4+} + e^{-} \longrightarrow Ce^{3+}$$
$$Fe^{3+} + e^{-} \longrightarrow Fe^{2+}$$

- Oxidation and reduction reactions always occur simultaneously; i.e. when one substance is oxidized the other substance is reduced and vice versa.

- *Generally, During a redox reaction the oxidizing agent itself undergoes reduction while the reducing agent undergoes its oxidation.*

- Thus reduction reaction is represented as
  - **Oxidant + ne = Reductant**

- Oxidation reaction is represented as
  - **Reductant = Oxidant + ne**

- The relative tendency to accept or lose electrons by any reagent is measured in terms of their standard reduction potential values.
- The standard electrode potential enable us to predict which ions will oxidize or reduce other ions.

- **Reduction potential** is a measure of **how thermodynamically favorable** it is for a cpd to **gain electrons**
- A high positive value for a reduction potential indicates that a cpd is readily reduced and consequently is a **strong oxidizing agent**, i.e.
  - A substance with a higher reduction potential will oxidize one with a lower reduction potential

Table: standard reduction potential (E_o) for some redox pairs relative to the **standard hydrogen electrode** potential

			E_o
$Ce^{4+} + e$	→	Ce^{3+}	1.61 V
$MnO_4^- + 5e + 8H^+$	→	$Mn^{2+} + 4H_2O$	1.51 V
$Cl_2 + 2e$	→	$2Cl^-$	1.36 V
$Br_2 + 2e$	→	$2Br^-$	1.065 V
$Fe^{3+} + e$	→	Fe^{2+}	0.771 V
$I_2 + 2e$	→	$2I^-$	0.536 V
$AgCl + e$	→	$Ag + Cl^-$	0.223 V
$2H^+ + 2e$	→	H_2	0 V
$Fe^{2+} + 2e$	→	Fe	-0.440 V
$Ca^{2+} + 2e$	→	Ca	-2.888 V

- The oxidized and reduced form of a substance are known as a redox pair

- The quantitative measurement of one of the reactants may be accomplished by the reaction derived from the combination of oxidizing and reducing agents

$$Fe^{2+} + Ce^{4+} \longrightarrow Fe^{3+} + Ce^{3+}$$

- and hence, **ferrous sulphate** can be estimated quantitatively by its reaction with **ceric sulphate**

❖ Balancing equations

- In order to make **analytical calculations**, which are based up on reaction stoichiometry, it is necessary to balance the reaction equation

- **Common steps followed in balancing:**
- e.g. the oxidation of hydrogen peroxide by permanganate in acid solution
  - permanganate half reaction (**Reduction**): $MnO_4^- \rightleftharpoons Mn^{2+}$
  - Hydrogen peroxide half rxn (**Oxidation**): $H_2O_2 \rightleftharpoons O_2$

- **Step 1**: Balance each half reaction both chemically and electrically
  - first **chemically**, by suitable addition of water and hydrogen ions
  - Then **electrically**, by adding an appropriate number of electrons

Reduction Half reaction

- Balance chemically
  - MnO_4^- ⇌ Mn^{2+}
  - MnO_4^- + 8 H^+ ⇌ Mn^{2+} + $4H_2O$
- Then balance electrically
  - MnO_4^- + 8 H^+ ⇌ Mn^{2+} + $4H_2O$
  - MnO_4^- + 8 H^+ + $5e^-$ ⇌ Mn^{2+} + $4H_2O$

Oxidation Half reaction

- Balance chemically
- H_2O_2 ⇌ O_2
- H_2O_2 ⇌ O_2 + $2H^+$

- Then balance electrically

H_2O_2 ⇌ O_2 + $2H^+$

H_2O_2 ⇌ O_2 + $2H^+$ + 2e-

- **Step 2**: equate the electron yield in the oxidation to the electron consumption in the reduction half reaction

- Since **5e-** were consumed in the balanced reduction half reaction, whereas **only 2e-** were produced from oxidation half rxn

  - Multiply the oxidation half reaction by 5/2 to yield 5e-

    - $5/2 H_2O_2 \rightleftharpoons 5/2\ O_2 + 5H^+ + 5e^-$

- **Step 3**: Add the half reaction, canceling e-,
  - $MnO_4^- + 8\ H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$
  - $5/2H_2O_2 \rightleftharpoons 5/2\ O_2 + 5H^+ + 5e^-$
  - $MnO_4^- + 3H^+ + 5/2H_2O_2 \rightleftharpoons Mn^{2+} + 4H_2O + 5/2\ O_2$
- **Step 4**: Reduce the coefficients to the whole numbers
  - $\mathbf{2MnO_4^- + 6H^+ + 5H_2O_2 \rightleftharpoons 2Mn^{2+} + 8H_2O + 5O_2}$

check

Mn	2	2
O	18	18
H	16	16
Charge	+4	+4

Redox titrations

- **These titrations involve simultaneous oxidation-reduction reactions.**
- It includes all the methods where in reacting substance is oxidized or reduced by the standard solution.
- In principle, redox titrations can be used to analyze for any oxidizing or reducing agent.
- **Limitation:**
  - **Many redox reactions are either too slow or have inconsistent stoichiometry.**
  - **The stability of titrant and analyte solutions can also be a problem.**
- Nevertheless, a wide variety of analytes can be conveniently determined by redox titrations.

- Some of the commonly used oxidizing and reducing agents in the redox titrations are

- Oxidizing agents

i. $KMnO_4$ in presence of dil H_2SO_4

$MnO_4^- + 8H+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ $E°red = +1.52V$

ii. $K_2Cr_2O_7$ in dil. H_2SO_4

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$ $E°red = +1.33V$

iii. $Ce(SO_4)_2$, $Ce(NO_3)_4$

$Ce^{4+} + e^- \rightarrow Ce^{3+}$ $E°red = +1.44V$

iv. Iodine solution

$I_2 + 2\ e^- \rightarrow 2I^-$ $E°red = +0.54V$

- Reducing agent

i. Mohr's salt $FeSO_4.(NH_4)_2SO_4.6H_2O$

$Fe^{2+} \rightarrow Fe^{3+} + e^-$ $E°red = +0.77V$

ii. Oxalic acid $H_2C_2O_4.2H_2O$

$C_2O_4^{2-} \rightarrow 2CO_2 + 2\ e^-$ $E°red = +0.77V$

iii. Sodium thiosulphate $Na_2S_2O_3.5H_2O$

$2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2\ e^-$ $E°red = +0.08V$

Method of detecting the end point

- Methods used for visual indication of the end point in a redox titration includes:
  - **Self Indicators**
  - **Redox indicator**
  - ***Other chemical indicators:***
  - Potentiometric Methods
  - Spectrophotometric titrations

1. Self indicators

- ✓ A few titrants, such as MnO^-_4, have oxidized and reduced forms whose colors in solution are significantly different.
- ✓ Solutions of MnO^-_4 are intensely purple.
- ✓ In acidic solutions, however, permanganate's reduced form, $\mathbf{Mn^{2+}}$, is nearly colorless.
- ✓ When MnO^-_4 is used as an oxidizing titrant, the solution remains colorless until the first drop of excess MnO^-_4 is added. The first permanent shade of purple signals the end point.

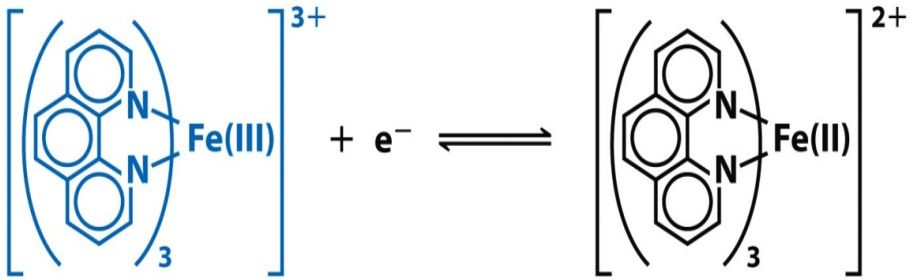
$$\underset{\text{(purple)}}{2\,MnO_4^-} + 5\,H_2C_2O_4 + 6\,H^+ \rightleftharpoons \underset{\text{(colorless)}}{10\,CO_2} + \underset{\text{(colorless)}}{2\,Mn^{2+}} + 8\,H_2O$$

2. Redox indicators

- A redox indicator is a compound which can undergo a redox reaction and change colour depending on the potential of the solution.
  - The oxidised and reduced forms of the indicator have different colours.
- When added to a solution containing the analyte, the indicator imparts a color that depends on the solution's electrochemical potential.
- Since the indicator changes color in response to the electrochemical potential, and not to the presence or absence of a specific species, these compounds are called general redox indicators.

Table Redox indicators

Indicator	Color		E°
	Oxidized	Reduced	
Phenosafranine	Red	Colorless	0.28
Indigo tetrasulfonate	Blue	Colorless	0.36
Methylene blue	Blue	Colorless	0.53
Diphenylamine	Violet	Colorless	0.75
4′-Ethoxy-2,4-diaminoazobenzene	Yellow	Red	0.76
Diphenylamine sulfonic acid	Red-violet	Colorless	0.85
Diphenylbenzidine sulfonic acid	Violet	Colorless	0.87
Tris(2,2′-bipyridine)iron	Pale blue	Red	1.120
Tris(1,10-phenanthroline)iron (ferroin)	Pale blue	Red	1.147
Tris(5-nitro-1,10-phenanthroline)iron	Pale blue	Red-violet	1.25
Tris(2,2′-bipyridine)ruthenium	Pale blue	Yellow	1.29



Oxidized ferroin (pale blue) In(oxidized)

Reduced ferroin (red) In(reduced)

$$\frac{[\text{In(reduced)}]}{[\text{In(oxidized)}]} \geq \frac{10}{1} \quad \text{or} \quad \frac{[\text{In(reduced)}]}{[\text{In(oxidized)}]} \leq \frac{1}{10}$$

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3. other indicators:

- ***Some indicators form a colored compound with a specific oxidized or reduced form of the titrant or the titrand***
- **Starch**, for example, forms a dark blue complex with I_3^- and can be used
  - to signal the presence of excess I_3^- (color change: colorless to blue), or
  - the completion of a reaction in which I_3^- is consumed (color change: blue to colorless).
- Another example of a specific indicator is **thiocyanate,** which forms a soluble red-colored complex, $Fe(SCN)^{2+}$, with Fe^{3+}.

Applications of redox titrations

- In oxidimetric titrations the oxidising agents are used to determine the reducing and while is reductimetric agents are employed for the determination of oxidising agents.

I. Oxidimetric Reagents

- Used for the analysis of reducing agents.
- The choice of oxidizing titrants is best for a particular analysis depends on the ease way with which the analyte can be oxidized.
- Analyte that are strong reducing agents can be successfully titrated with a relatively weak oxidizing titrant, whereas a strong oxidizing titrant is required for the analysis of analyte that are weak reducing agents.

- These are classified as

1) Permanganimetric: Titrant $KMnO_4$

2) Dichromatometric: Titrant $K_2Cr_2O_7$

3) Cerimetric titration: Titrant $Ce(SO_4)_2$

4) Titrations involving iodine (I_2)

   - Iodimetry
   - Iodometry

5) Iodatometric titrations: KIO_3

6) Bromatometric titrations: $KBrO_3$

Applications

- Oxidizing agents are used as a titrant to determine the reducing agent and reducing agents are employed as a titrant for the determination of oxidizing agents.

1. **Permanganimetric:Titrant $KMnO_4$**

- A MnO_4^- (VII) are readily reduced to form Mn^{2+} in acidic conditions
  - $8H^+ + MnO_4^- + 5e \longrightarrow Mn^{2+} + 4H_2O$
  - It is useful oxidizing agent as MnO_4^- **Ions have different colors (purple) that of Mn^{2+}(colorless)**

- **C**an be used for the analysis of many reducing agents.
- Examples
  - Determination of peroxide: eg. Hydrogen peroxide, ZnO_2
  - Determination of ferrous salt

E.g. to determine the concentration of Fe^{2+}

- Equation:

$$8H^+ MnO_4^- + 5Fe^{2+} \longrightarrow Mn^{2+} + H_2O + 5Fe^3$$

- Until the end point, our analyte will remain colorless.

- **Example:** 21.6 ml of 0.015 M of $KMnO_4$ is added to 30 ml of solution containing an unknown amount of iron (II) ions until the purple color is detected.

- Q1. What was the concentration of iron (II) in the solution before titration?

Answer: 0.0054 M

Q1. The purity of a sample of sodium oxalate, $Na_2C_2O_4$, (M.wt= 134 g/mol) is determined by titrating with a standard solution of $KMnO_4$. A 0.5116 g sample was titrated by 0.0400 M $KMnO_4$ and consumed 35.62 mL to reach the titration's end point, what is the %w/w $Na_2C_2O_4$ in the sample.

Reduction Half reaction

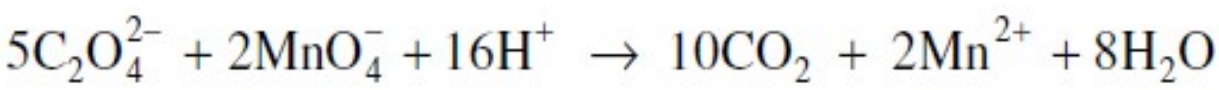
$$MnO_4^- \rightleftharpoons Mn^{2+}$$

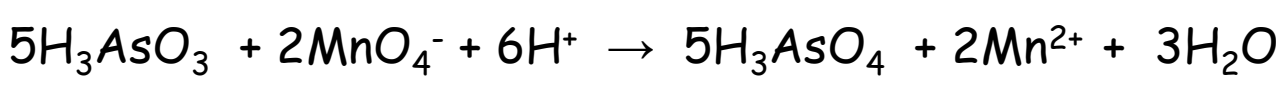
Oxidation Half reaction

$$C_2O_4^{2-} \rightleftharpoons 2CO_2$$

☞ **Answer: 93.3%**

- **Limitation:**
  - ✓ KMnO4 **not** being a primary standard.
  - ✓ An aqueous solution of permanganate is thermodynamically unstable due to its ability to oxidize water, catalyzed by light and heat
  - ✓So, solution needs to be **stored in dark**
- The solution of KMnO4 is standardised against a primary standard (sodium oxalate , Arsenic acid).





2. Potassium dichromate

- It is a strong oxidant in acidic medium; the reduction equation being the following.

$$Cr_2O_7^{2-} + 14H^+ + 6e \rightleftharpoons 2Cr^{3+} + 7H_2O;\ E^0 = 1.33\ V$$

+VI (Orange) ⇌ +III (green)

- it can't be used as a self indicator like $KMnO_4$
- The end point in titrations with dichromate ion is generally detected by using suitable redox indicators such as
  - diphenylamine,
  - sodium diphenylaminesulphonate

- Potassium dichromate possesses an advantage over permanganate.

- Potassium dichromate is a primary standard and is obtainable in a high state of purity.
  - Its standard solution can, therefore, be prepared by direct weighing.

- The aqueous solutions are quite stable towards light
- It does not oxidise chloride ion
  - Thus it can be used to determine iron(II) in hydrochloric acid medium

3. Cerium (IV) salts

- Cerium (IV) sulphate is a powerful oxidising agent in acidic medium.

Yellow $Ce^{4+} + e \rightarrow Ce^{3+}$ **colorless**

- Ceric sulphate available in pure state and solutions are remarkably stable.
  - Cerium(IV) solution may be prepared by dissolving Cerium(IV) sulphate

❑ **Application:** almost anything that can be done with potassium permanganate can be done more conveniently with ceric sulfate. This include:

- ❑ Determination of Iron (Fe^{2+}) in ferrous gluconate, ferrous fumerate, ferrous sulphate,etc
- ❑ Drugs having quinone functional group
- ❑ Acetaminophene

4. Iodimetric and Iodometric methods

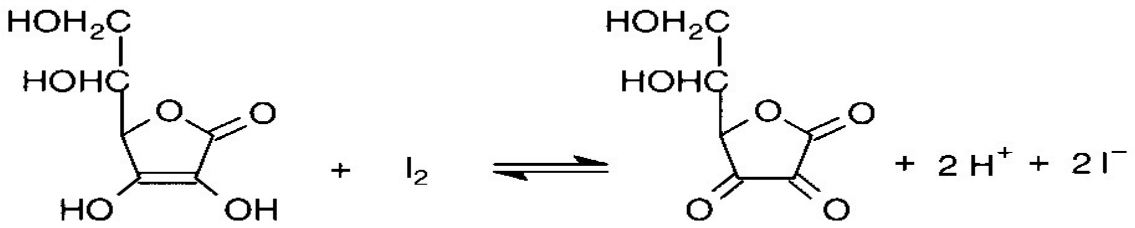
- oxidation-reduction titrations wherein
  - either **iodine** solutions are employed **directly** for the assay or
  - an equivalent amount of iodine is liberated indirectly from the reaction mixture and then assayed

$I_2 + 2e \longrightarrow 2I^-$ → Iodimetric

$2I^- \longrightarrow I_2 + 2e$ → Iodometric

➢There are two classes of titrations involving iodine:

1. ***Iodimetry,*** which is based on the direct reaction between the analyte and iodine. Since iodine is an oxidizing agent, iodimetry is used for the analysis of reductants (reducing agents).



Oxidation of ascorbic acid by iodine.

Ascorbic acid

- The endpoint is indicated by the reaction of iodine with starch suspension, which produces a blue-black product.
  - As long as vitamin C is present, the **triiodide** is quickly converted to **iodide ion**, and **no blue-black iodine-starch product is observed.**
  - However, when all the vitamin C has been oxidized, the **excess triiodide** (in equilibrium with iodine) **reacts with starch** to form the expected **blue-black color.**

2. Iodometry: *which is based on the reaction between the analyte and unmeasured excess of* iodide to *produce iodine, which is measured by titration with thiosulfate.*

- ✓ The amount of iodine produced by this reaction is stiochiometrically related to the amount of analyte originally present in the solution.
- ✓ Since iodide is a reductant, *iodometry is used for the analysis of oxidants.*
- ✓ Many oxidants are capable of converting iodide quantitatively to free iodine which can be titrated with a standard solution of sodium thiosulphate.

$$Ox + I^- \rightleftharpoons I_2 + Red$$

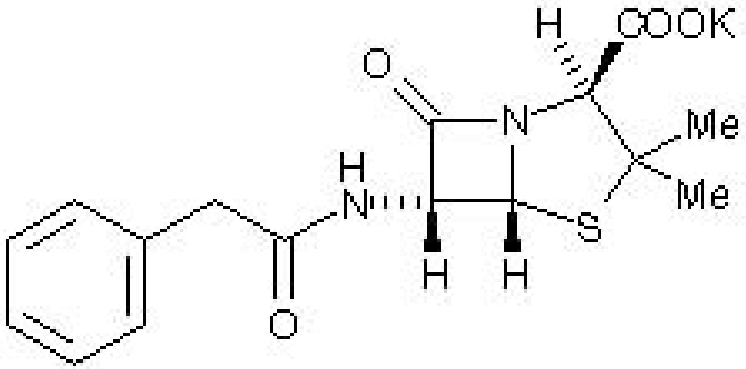
$$I_2 + 2S_2O_3^{2-} \rightleftharpoons 2I^- + S_4O_6^{2-}$$

Summary:

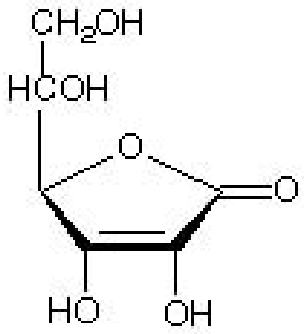
- **Iodimetric titrations:**
  - ✓ Used to detrmie a reducing analyte
  - ✓ One step reaction
  - ✓ Standard solution: Iodine (I_2)
- **Iodometric titrations:**
  - ➢ Used to determine an oxidizing analyte
  - ➢ Two step reactions
  - ➢ Standard solution: Sodium thiosulfate

Drugs direct titrated with standard iodine solution:

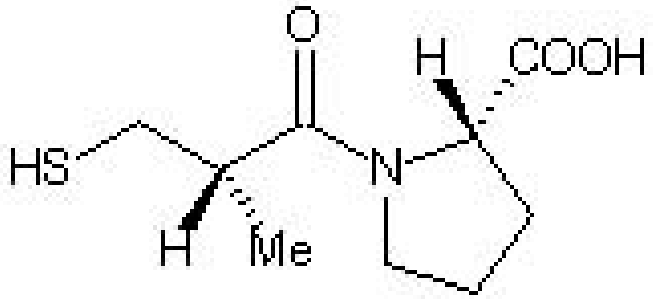
Benzylpencillin potassium



Ascorbic acid



Captopril



- The amount of ascorbic acid, $C_6H_8O_6$, in orange juice was determined by oxidizing the ascorbic acid to dehydroascorbic acid, $C_6H_6O_6$, with a known excess of I_3^- and back titrating the excess I_3^- with $Na_2S_2O_3$.
- A 5.00-mL sample of filtered orange juice was treated with 50.00 mL of excess 0.01023 M I_3^-. After the oxidation was complete, 13.82 mL of 0.07203 M $Na_2S_2O_3$ was needed to reach the starch indicator end point. Report the concentration of ascorbic acid in milligrams per 100 mL.

A. $C_6H_8O_6 + I_3^- \text{ (excess)} \rightarrow C_çH_6O_6 + 3I^- + 2H^+$

B. $$I_3^- + 2S_2O_3^{2-} = 3I^- + S_4O_6^{2-}$$

The total moles of I_3^- used in the analysis is the sum of that reacting with ascorbic acid and $S_2O_3^{2-}$

$$(\text{Moles } I_3^-)_{\text{tot}} = (\text{moles } I_3^-)_{\text{ascorbic acid}} + (\text{moles } I_3^-)_{\text{back titration}}$$

or

$$\text{Moles } I_3^- = \text{moles } C_6H_8O_6 + 0.5 \times \text{moles } S_2O_3^{2-}$$

Making appropriate substitutions for the moles of I_3^-, $C_6H_8O_6$, and $S_2O_3^{2-}$

$$M_{I_3^-} \times V_{I_3^-} = \frac{\text{g } C_6H_8O_6}{\text{FW } C_6H_8O_6} + 0.5 \times M_{S_2O_3^{2-}} \times V_{S_2O_3^{2-}}$$

and solving for the grams of $C_6H_8O_6$ gives

$$(M_{I_3^-} \times V_{I_3^-} - 0.5 \times M_{S_2O_3^{2-}} \times V_{S_2O_3^{2-}}) \times \text{FW } C_6H_8O_6 =$$

$$[(0.01023\text{ M})(0.0500\text{ L}) - (0.5)(0.07203\text{ M})(0.01382\text{ L})](176.13\text{ g/mol})$$

$$= 0.00243\text{ g } C_6H_8O_6$$

Thus, there is 2.43 mg of ascorbic acid in the 5.00-mL sample, or 48.6 mg/100 mL of orange juice.

II. Reductimetric Reagents

- Standard solutions of reducing agents are **not** used as widely as oxidising agents, because most of them are **oxidised by dissolved and atmospheric oxygen.**
- The two most common reducing titrants are ferrous ammonium sulfate (FAS) and sodium thiosulfate.
  - Thiosulphate is the only common reducing agent that is stable to air oxidation and can be kept for long periods of time.
- Procedures using these titrants are capable of determining the concentrations of analytes that are (at least) moderately strong oxidizing agents.

The end of redox titration